REMARKS

The Office action dated September 22, 2010, and the references cited therein have been received and carefully reviewed.

The objections to claims 25 and claims 2-7, 18, and 22-28 are obvated by appropriate amendment. Specifically, claim 25 has been canceled. Furthermore, a comma has been inserted after "solvent" in claim 22, seven lines from the bottom of the claim.

Favorable reconsideration and withdrawal of the objections to the claims is thus respectfully urged.

The rejection of claim 23 under 35 U.S.C. §112, second paragraph, is obviated by appropriate amendment. Specifically, the term "partly or entirely" has been canceled from claim 23. Furthermore, claim 22 has been partly amended to clarify the language of the claim, in general accordance with the Examiner's suggestion.

Accordingly, it is believed that the rejection of claims 23 and 2-7, 18, and 22-28 under 35 U.S.C. §112, second paragraph, has been overcome. Favorable reconsideration and withdrawal of the rejection is thus respectfully urged.

Claims 7, 18, 22-25, 27, and 28 have been rejected under 35 U.S.C. 103(a) as being unpatentable over Krass et al.; Claims 7, 18, and 22-28 have been rejected under 35 U.S.C. 103(a) as being

unpatentable over Krass et al. in view of Sakamoto et al.;

Claims 2-7 have been rejected under 35 U.S.C. 103(a) as being

unpatentable over Hata et al.; and claims 2-7 have been rejected

under 35 U.S.C. 103(a) as being unpatentable over Krass et al.

in view of Sakamoto et al. and Hata et al.

It is submitted that the present claims, as amended, are

not disclosed or suggested by the cited prior art references.

Favorable reconsideration of these rejections is thus

respectfully urged, for the following reasons.

The Examiner maintains his opinion that the invention

defined by claim 22 is obvious in view of Krass et al. alone or

in combination with Sakamoto. The Applicant respectfully

disagrees.

The present claims differ from the prior art in the way the

epoxy hardener is prepared. By removing the volatile reaction

products and solvents in the present invention, it is ensured

that the sol-gel product is stable and condensed.

The enclosed manuscript abstract by Männle et al., and the

corresponding publication, show that this concerns polyhedral

oligomeric silsesquioxanes, which are not silica nanoparticles

as discussed by Krass et al. The publication shows details on

the structure of the above mentioned polyhedral oligomeric

silsesquioxanes (especially p. 4 of the publication).

8

Furthermore, a comprehensive review on polyhedral oligomeric silsesquioxanes is given in Cordes et al., which is cited in the publication.

The sol according to the present invention is stable immediately after manufacturing as mentioned several times in the application. The sol of Krass et al. is not stable immediately after synthesis, and requires therefore a maturing time of three days after ending preduction. This clearly indicates that the product substantially does not consist of polyhedral oligomeric silsesquioxanes, which would not change and mature during a shelf-time of three days.

It is also important to note that the removal of the solvent is a sophisticated process and cannot easily be performed by a person skilled in the art without knowledge of the present application. Before the right process parameters were discovered during the development of the present invention, the sol was easily cross-linked or precipitated, leaving a useless non-soluble material back. This explains why the solvent removal and formation of polyhedral oligomeric silsesquioxanes has not been published before the present application was filed.

In view of all of the above, it is submitted that the invention of claim 22, as amended, and claims dependent thereon,

is not disclosed or suggested by the prior art of record. Favorable reconsideration of the rejections under 35 U.S.C. 103(a) is thus respectfully urged.

Applicants traverse the provisional rejection of claims 2-7, 22, 23, and 26-28 on the ground of nonstatutory obviousness-type double patenting as being unpatentable over the combined limitations of claims 1-3, and 5-17 of US 2007/0290176; the provisional rejection of claims 2-4, 7, 18, and 22-28 on the ground of nonstatutory obviousness-type double patenting as being unpatentable over the combined limitations of claims 1-24, 26, and 27 of US 2007/0260030; and the provisional rejection of claims 2-4, 7, 18, and 22-28 on the ground of nonstatutory obviousness-type double patenting as being unpatentable over the combined limitations of claims 1, 2, and 4 of US 2008/0039607.

Each of the cited applications were filed (and published) after Applicants' October 16, 2002, invention date, and are therefore not prior art. Clearly, neither of the cited publications discloses a hardener for curing epoxy resins or a method for curing epoxy resins, as presently claimed.
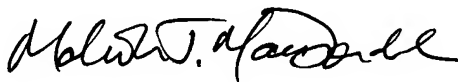
As such, the provisional rejections are unsustainable and should be withdrawn.

Applicants submit that the present application is now in condition for allowance and early notice of such action is

earnestly solicited. If any final points remain that can be clarified by telephone, Examiner Feely is respectfully encouraged to contact Applicants' attorney at the number indicated below.

Applicants hereby petition the Commissioner for Patents to extend the time for reply to the notice dated September 22, 2010, for three (3) months from December 22, 2010, to March 22, 2011. A duly completed Credit Card Payment form is attached to effect payment of the extension fee.

Respectfully submitted

Date: March 22, 2011   Malcolm J. MacDonald
                                    Reg. No. 40250

Manuscript Number:

Title: Polymer nanocomposite coatings based on polyhedral oligosilsesquioxanes - route for industrial manufacturing and barrier properties -

Article Type: Original research

Keywords: nanocomposite, POSS, synthesis, hybrid polymer, industrial manufacturing, barrier properties

Corresponding Author: Monika Pilz

Corresponding Author's Institution: SINTEF Materials & Chemistry

First Author: Ferdinand Männle

Order of Authors: Ferdinand Männle;Terje Tøfteberg;Morten Skaugen;Huaitian Bu;Thijs Peters;Pascal D. C. Dietzel;Monika Pilz

Abstract: A route to a large variety of functionalized POSS compounds by a two step procedure has been developed. Up-scaling to high volume industrial applications is feasible. In the first step an amino-functionalized silane such as 3-aminopropyltriethoxy silane is converted to amino-functionalized POSS (amine-POSS) by a sol-gel process. In the second step the amine groups of amine-POSS are converted by state-of-the-art amine chemistry. A large number of reactants including carboxylic acids, esters, anhydrides, isocyanates, carbonates, epoxides, and acrylates as well as reactants suitable for nucleophilic substitution can be applied.
Conversion of an amine-POSS with hexanoic acid leads to an amide-POSS. Amine chemistry can usually be performed under mild conditions, which suppresses degradation and / or cross-linking reactions of the amine-POSS during the conversion. MALDI-TOF mass spectroscopy and dynamic light scattering have been applied to prove the conversion of an amine-POSS to an amide-POSS. 1H-NMR and TGA-MS prove the presence of amide-POSS and its thermal stability. Gas barrier properties of nanocomposite coatings based on functionalized POSS are characterized.

Polymer nanocomposite coatings

based on polyhedral oligosilsesquioxanes

- route for industrial manufacturing and barrier properties -

Ferdinand Männle · Terje Tofteberg · Morten Skaugen · Huaitian Bu · Thijs Peters · Pascal D. C. Dietzel · Monika Pilz

F. Männle, T. Tofteberg, , H. Bu, T. Peters, P.D.C. Dietzel, M. Pilz

SINTEF Materials and Chemistry, Forskningsveien 1, NO-0373 Oslo, Norway

e-mail: monika.pilz@sintef.no, ferdinand.mannle@sintef.no

Morten Skaugen

Norwegian University of Life Sciences, NO-1432 Ås, Norway

Abstract A route to a large variety of functionalized POSS compounds by a two step procedure has been developed. Up-scaling to high volume industrial applications is feasible. In the first step an amino-functionalized silane such as 3-aminopropyltriethoxy silane is converted to amino-functionalized POSS (amine-POSS) by a sol-gel process. In the second step the amine groups of amine-POSS are converted by state-of-the-art amine chemistry. A large number of reactants including carboxylic acids, esters, anhydrides, isocyanates, carbonates, epoxides, and acrylates as well as reactants suitable for nucleophilic substitution can be applied.

Conversion of an amine-POSS with hexanoic acid leads to an amide-POSS. Amine chemistry can usually be performed under mild conditions, which suppresses degradation and / or cross-linking reactions of the amine-POSS during the conversion. MALDI-TOF mass spectroscopy and dynamic light scattering have been applied to prove the conversion of an amine-POSS to an amide-POSS. ^{1}H-NMR and TGA-MS prove the presence of amide-POSS and its thermal stability. Gas barrier properties of nanocomposite coatings based on functionalized POSS are characterized.

Keywords nanocomposite, POSS, synthesis, hybrid polymer, industrial manufacturing, barrier properties

Introduction

Organic/inorganic hybrid polymers based on polyhedral oligomeric silsequioxanes (POSS) face increasing interest. POSS polymers are composed of a robust silicon-oxygen framework with a diameter of about 1.5 nm that can be functionalized with a variety of organic substituents. Appropriate functionalization of POSS polymers allows their incorporation in traditional polymer products. A considerable number of applications in thermoplastics (Fina et al.2008, Iwamura et al. 2009, Kim et al. 2008, Liu et al.2008, Sanchez-Soto et al. 2009, Wan et al. 2009, Zhang et al. 2009, Zhou et al. 2008) thermosets (Glodek et al. 2008, Li et al. 2008, Zhang et al. 2007c, Zhang et al. 2007d, Zhang et al. 2007e), coatings (Amerio et al. 2008, Kim et al. 2009, Mabry et al. 2008), porous materials (Su et al. 2009, Zhang et al. 2007a) medicine (Kannan et al. 2005, Kidane et al. 2007, Wheeler et al. 2006, Wu et al. 2009) and light emitting polymers (Xiao et al. 2010) have been published recently. POSS as a component in polymer blends is used to improve tensile properties, impact strength, heat stability, gas barrier properties and rheological properties. For most applications POSS compounds are manufactured by controlled hydrolysis and condensation of suitable functionalized silanes (sol-gel process). In order to obtain the desired organic branches on the POSS molecules silanes available with exactly these organic groups have to be used (Haas et al. 2003). A major drawback of this manufacturing method is the need of specifically modified silanes for each type of POSS. Since few organic silanes are produced in a large scale the use of this manufacturing method for high volume industrial applications such as food packaging or automotive is limited. In a few cases the organic branches on POSS molecules can be further modified by selected chemical reagents. However, these processes yield a rather limited selection of modified POSS compounds (Lichtenhan et al. 1995, Schwab et al.1998). A comprehensive review on synthesis and properties of POSS has recently been published (Cordes et al. 2010). However, none of the preparation methods in this review has been up-scaled for high volume industrial applications.

Four patent applications have been filed in 2004 and 2005 disclosing the preparation and use of polybranched organic/inorganic hybrid polymers (Männle et al.2004a; Männle et al. 2004b, Männle et al. 2004c, Männle et al. 2005). The polybranched organic/inorganic hybrid polymers are synthesized by controlled hydrolysis and condensation of 3-

chemistry. The chemical structure of the obtained hybrid polymers has not been investigated and published in the patent work or previous publications (Pilz et al. 2009a, Pilz et al. 2009b). In this publication we fill this gap by studying a typical synthesis of polybranched organic/inorganic hybrid polymers in order to show that mainly POSS compounds are formed. A novel route to a large variety of functionalized POSS compounds by a two step procedure is therefore feasible. In the first step an amino functionalized silane is converted to amino functionalized POSS (amine-POSS) by a sol-gel process. In the second step the organic branches of amine-POSS are extended by state-of-the-art amine chemistry.

From an industrial point of view POSS products can be interesting components in polymer products if their benefit is not spoiled by too high manufacturing costs. The use of low cost organic commodities such as fatty acids decreases the manufacturing costs. Very recently, a POSS containing alkyd paint with reduced VOC and improved weathering resistance in northern climate has been introduced to the market (Helland et al. 2009). Barrier properties of polymer nanocomposite coatings based on functionalized POSS are now characterized by gas transmission rates of oxygen and helium to show the potential of those coatings for industrial packaging applications.

Experimental section

Synthesis of polyhedral oligosilsesquioxanes

Step 1: Amine-POSS. 221.4 g (1.00 mole) 3-aminopropyltriethoxysilane is placed in a 1000 ml flask equipped with reflux cooler and magnetic stirring under nitrogen atmosphere. A mixture of 64.9 g (0.60 mole) 1-propoxy-2-propanol and 22.5 g (1.30 mole) water is added. The mixture is warmed up and refluxed at 80 °C for 45 minutes. Thereafter, volatile products and the solvent are removed by vacuum distillation with the final pressure 20 mbar and temperature 150 °C. The product is cooled to 120 °C and diluted with 1-propoxy-2-propanol in order to yield a 50 % solution of amine-POSS in 1-propoxy-2-propanol.

Step 2: Amide-POSS. 63.9 g (0.55 mole) hexanoic acid (reactant) and 63.9 g 1-propoxy-2-propanol are heated to 150 °C. 118 g of a 50 % solution of amine-POSS in 1-propoxy-2-propanol (0.50 mole amine-POSS) is added within 30 minutes while water as well as 1-propoxy-2-propanol are distilled off. After the addition of amine-POSS is finished, the pressure is stepwise reduced to 20 mbar and water and 1-propoxy-2-propanol are distilled of. To remove residues of 1-propoxy-2-propanol the product is dissolved in ethanol under heating and the solvent is removed by vacuum drying (final pressure: 10^{-3} mbar).

Characteriseration of polyhedral oligosilsesquioxanes

^{1}H-NMR (300 MHz, Varian Gemini, DMSO-d$_6$). -Si-CH_2- 0.53 ppm, -CH$_2$-CH_3 0.85 ppm, -C(O)-CH$_2$-CH$_2$-CH_2- / -CH_2-CH$_3$ (overlapping) 1.24 ppm, -Si-CH$_2$-CH_2- / -C(O)-CH$_2$-CH_2- (overlapping) 1.46 ppm, -C(O)-CH_2- 2.05 ppm, -Si-CH$_2$-CH$_2$-CH_2- 3.00 ppm, -HN-C(O)- 7.84 ppm.

MALDI-TOF. A solution of 1 % v/v of amide-POSS in 2-metoxy propan-1-ol was mixed in a ratio 1:1 v/v with matrix solution. The matrix solution consisted of 15 mg/ml 2,5-dihydroxybenzoic acid and 2-hydroxy-5-methoxybenzoic acid (sDHB, Bruker Daltonics, Bremen, Germany) dissolved in a mixture of trifluoroacetic acid (0.1 % v/v), de-ionized water (49.9 % v/v) and ethanol (50 % v/v). The so prepared sample was applied directly on the MALDI target (Bruker Daltonics ground steel). The instrument (Ultraflex TOF/TOF, Bruker Daltonics) was operated at an acceleration voltage 25 kV with delayed ion extraction 40 ms using a 337 nm N$_2$ laser.

Dynamic light scattering. The setup for the dynamic light scattering (DLS) experiments is an ALV/CGS-8F multidetector version compact goniometer system, with eight fiber-optical detection units from ALV-GmbH, Langen, Germany. The light source is a Uniphase cylindrical 22 mW HeNe-laser operating at a wavelength of 632.8 nm with vertically polarized light. The beam was focused on the sample cell (10 mm NMR tubes, Wilmad Glass Co., of highest quality) through a temperature-controlled cylindrical quartz container (temperature controlled to within ± 0.05 °C), which is filled with a refractive index matching liquid (cis-decalin). The correlation function was measured at eight scattering angles simultaneously in the range 22-141 ° with four ALV 5000/E multiple-τ digital correlators. DLS measurements were performed on 10 wt% solutions of amine-POSS and amide-POSS in 1-propoxy-2-propanol to determine the hydrodynamic radius of the two particles. The relaxation times were deduced from the correlation function and are q^2-dependent. The diffusion coefficient (D_m) was then calculated according to Eq. 1

$$D_m = (\tau_f q^2)^{-1}.$$ (1)

In Eq. 1 τ_f is the mean relaxation time and q the wave vector. The hydrodynamic radius for the two particles in solution was calculated using the Stokes-Einstein relation.

Thermogravimetric analysis and mass spectroscopy (TGA-MS). TGA-MS was performed on a STA 449 F1-QMS (Netzsch, Germany). The heating rate was 2 °C/min under nitrogen atmosphere. The QMS mass range is 300 amu with

Gas barrier measurements. The oxygen transmission rate (OTR) has been measured at standard conditions (23 °C, 50 %RH) with an OX-TRAN® Model 2/10. Measurements to determine helium transmission rate (HeTR) were performed in an in-house built membrane-like set-up. A back pressure controller (Bronkhorst High-Tech) was used to pressurize the helium feed up to 2.0, 3.0 and 4.0 bar, while Argon was applied at the permeate side. A μ-GC (Varian CP4900) was employed to monitor the permeate composition. Fluxes were calculated from the measured permeate He concentration and the calibrated flow of argon sweep gas.

Results and discussions

Polyhedral oligosilsesquioxanes: amine-POSS and amide-POSS

Amine-POSS. The conversion of 3-aminopropyltriethoxy silane (APS) to amine-POSS is shown in Fig. 1. In order to reduce the amount of unreacted Si-OCH2-CH3 and Si-OH intermediates the amine-POSS is heated in 1-propoxy-2-propanol to 150 °C and the solvent is removed by vacuum distillation. The amount of free amine groups is measured as amine equivalents by titration with hydrochloric acid. The product has an amine number of 118 g/eq which is quite close to the calculated value of 111 g/eq. The deviation can be explained by a suppressed degradation of amine groups during the process and the presence of solvent residues.
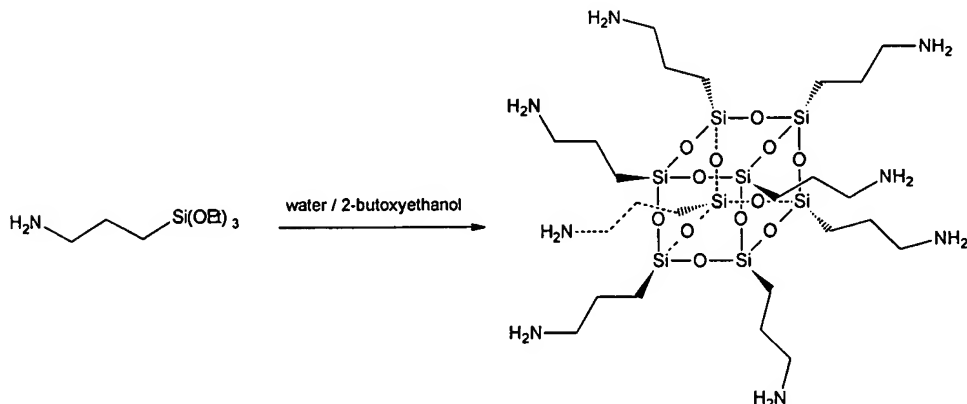

Fig. 1 Synthesis of amine-POSS by a sol-gel process (step 1)

Amide-POSS. Fig. 2 shows the conversion of amine-POSS with hexanoic acid to amide-POSS. The product is soluble in mixtures of water and 2-butoxyethanol and titration shows no unreacted amine groups. Instead of hexanoic acid a large number of reactants including other carboxylic acids, esters, anhydrides, isocyanates, carbonates, epoxides, and acrylates as well as reactants suitable for nucleophilic substitution can be applied. This opens up versatile applications and materials based on POSS. Amine chemistry can usually be performed under mild conditions which limit the degradation and/or cross-linking of amine-POSS.
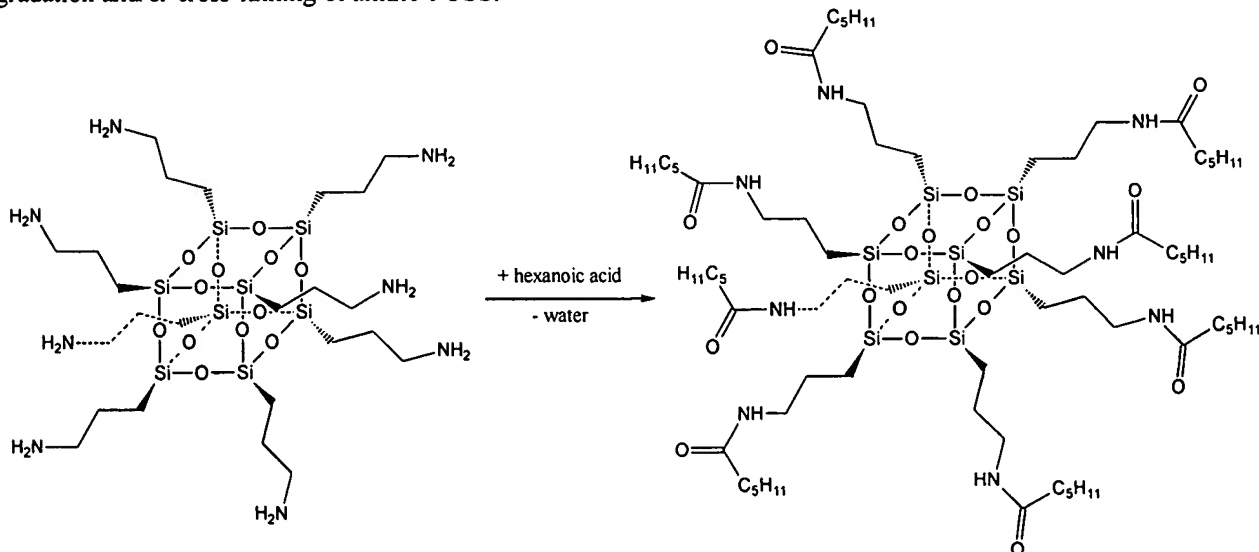

Fig. 2 Synthesis of amide-POSS by reaction of amine-POSS with hexanoic acid (step 2)

MALDI-TOF

The method of choice to measure the molecular weight of POSS compounds is MALDI-TOF. This has been demonstrated previously (dell' Erba et al. 2003, Manson et al. 2001, Smentkowski et al. 2006, Sheen et al. 2008).
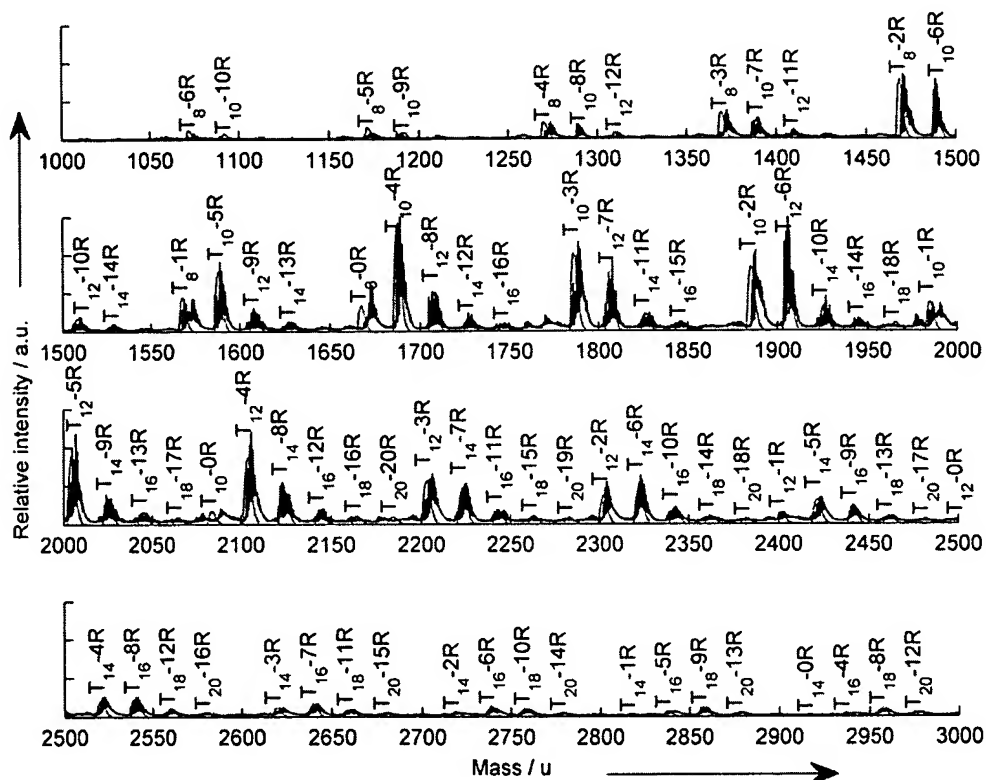

Fig. 3 MALDI-TOF mass spectrum of amide-POSS (blue) compared with the theoretical isotope distribution (red)

MALDI-TOF of amide-POSS (Fig. 3) shows the presence of T_8, T_{10} and T_{12} POSS which is in compliance with earlier findings (dell' Erba et al. 2003, Zhang et al. 2007b).
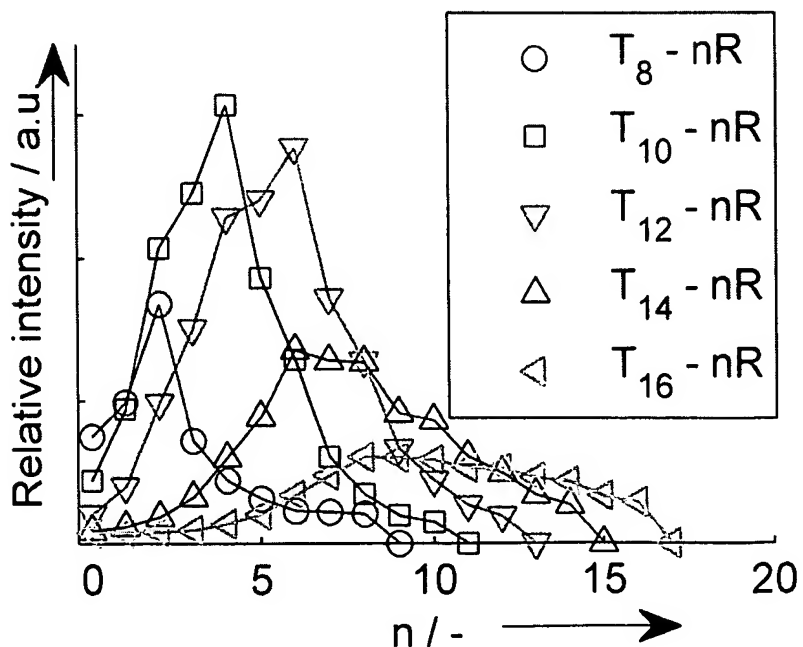

Fig. 4 Integrated intensity of the peaks based on the MALDI-TOF mass spectrum of amide-POSS as shown in Fig. 3

Larger POSS molecules are present in minor amounts. The assignment of the MALDI-TOF peaks is based on the assumption that the amide-POSS partly loose hexanoyl groups during laser desorption ionisation. A possible explanation is the formation of agglomerates due to strong hydrogen bondings between the amide groups which partially leads to bond cleavage during desorption. Hydrolysis during sample preparation and desorption is unlikely since these processes are performed within five minutes. On this background we assume that each peak can be attributed to a molecule on the form $T_{2m} - R_n$, where R is $CO(CH_2)_4CH_3$. For all m equal 4 to 10 and for all n equal 1 to m, the theoretical isotope distribution of the molecule $T_{2m} - R_n$ is calculated and shown together with the mass spectrum in Fig. 3. It can be seen that all peaks in the spectrum can be accounted for by this assumption.

The integral of each peak is shown as a function of n and m (Fig. 4). It can be seen that the most common products are the T_{10} and the T_{12}, but also smaller amounts of T_8, T_{14} and T_{16} are present. It can also be seen that within each T_{2m} series the most abundant molecule is missing approximately half of the R groups, with the abundance falling to each side of the central value.

Dynamic light scattering

The particle size increase resulting from the conversion of amine-POSS to amide-POSS has also been demonstrated by dynamic light scattering. Fig. 5 depicts the correlation functions of amine-POSS and amide-POSS at a scattering angle of 90 °. As can be seen from Fig. 5, the correlation function shifts to longer times when the amine-POSS was modified by hexanoic acid and converted into amide-POSS. This indicates that the diffusion of the particles becomes slower. Both systems are diffusive with narrow distribution of relation time, implying the homogeneous size distributions of both amine-POSS and amide-POSS. The diffusion coefficient (D_m) was then calculated as described in the experimental section. The hydrodynamic radius of amine-POSS and amide-POSS are 1.7 nm and 2.7 nm, respectively. The difference is in good compliance with the length of a hexanoyl group which is between 0.8 and 0.9 nm. Therefore the increase indicates the conversion of amine groups to the considerably larger hexanoic amide groups.
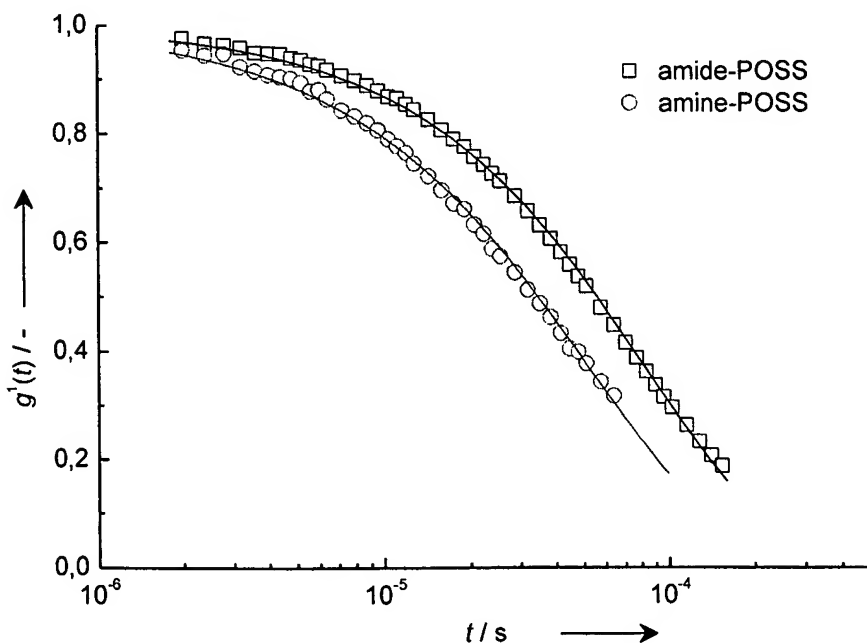

Fig. 5 DLS correlation functions for amine-POSS and amide-POSS in 1-propoxy-2-propanol - solid lines show a fit of the correlation function to a stretched exponential function $\log g^1(t) = -(t/\tau_f)^\beta$

^{1}H-NMR

The ^{1}H-NMR spectrum in Fig. 6 indicates a high purity of the amide-POSS. Visible impurities are small amounts of ethanol which was used for sample preparation and the reactant hexanoic acid which was used in excess. The α-CH$_2$-resonance of hexanoic acid in the presence of amide-POSS is shifted to high field which can be explained by a different chemical environment due to hydrogen bonding (Limbach 2007).
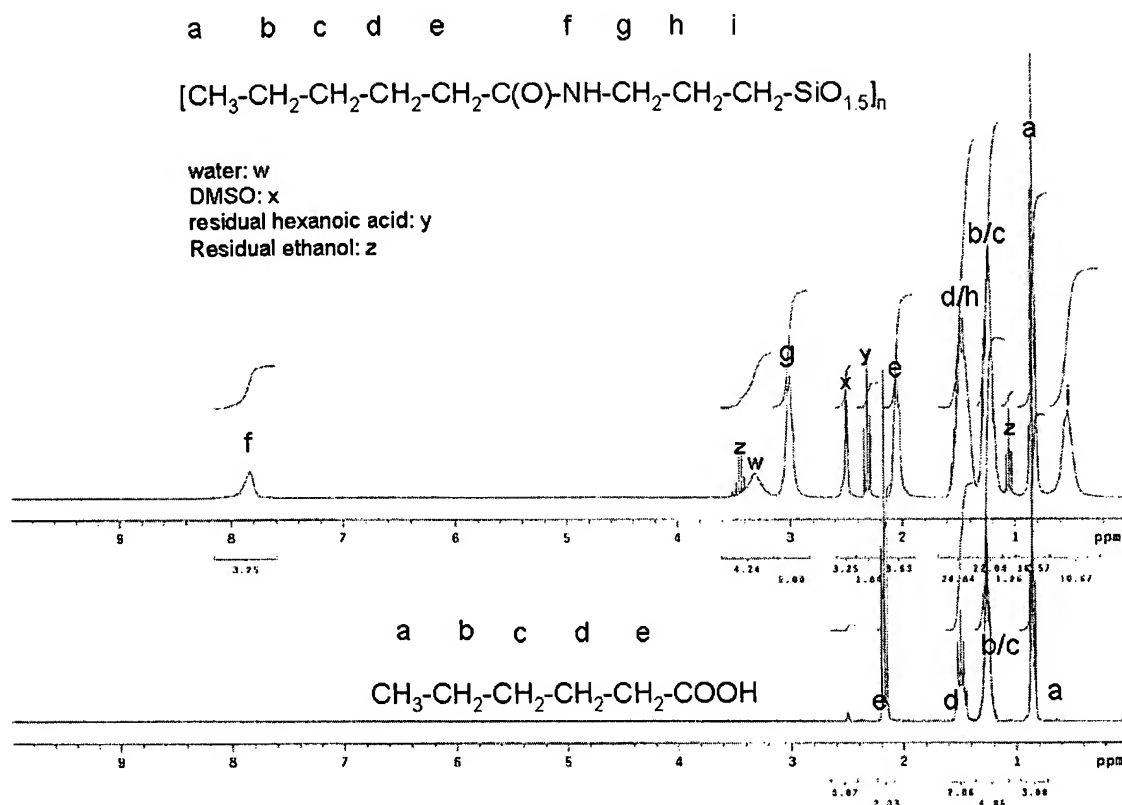
a   b   c   d   e   f   g   h   i

$[CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}C(O)\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}SiO_{1.5}]_n$

water: w
DMSO: x
residual hexanoic acid: y
Residual ethanol: z

a   b   c   d   e

$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}COOH$

Fig. 6 ^{1}H-NMR spectra of reactant hexanoic acid (below) and amide-POSS (above)

TGA-MS

The presence of free hexanoic acid is also shown in the TGA-MS analysis (Fig. 7). Water (m/z = 18) and hexanoic acid (m/z = 60) are evaporated below 200 °C. Severe degradation starts right below 400 °C. The DSC-line between the mass traces shows that both processes are endothermic. Thermal stability is of the essence when POSS is blended into polymers by using melt processes.
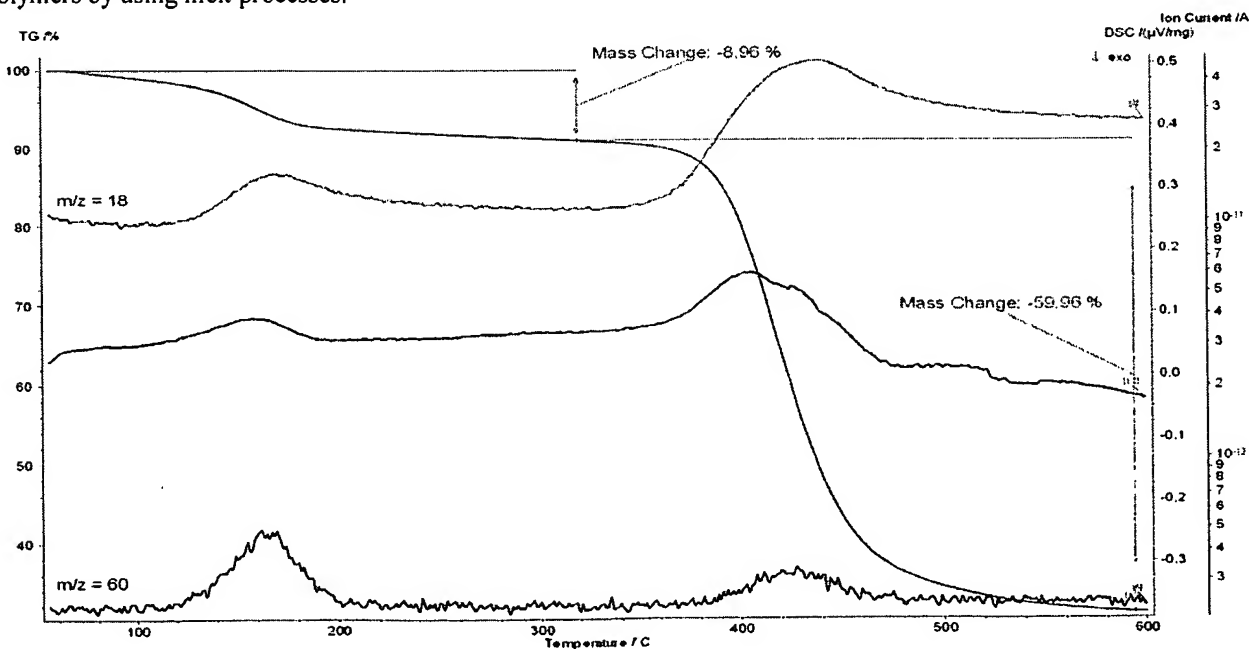

Fig. 7 TGA-MS analysis of amide POSS

Selection of functionalized POSS prepared by the two step procedure

Several types of functionalized POSS have been prepared by the two step procedure and presented in Table 1.

Table 1 Selected qualities of FunzioNano®

Derivative	Reactant	Chemical functionality
Amine-POSS	None	Primary amine
FunzioNano-1	Hexanoic acid	Amide
FunzioNano-2	Mixture of unsaturated fatty acids	Amide
FunzioNano-3	Salicylic acid	Amide
FunzioNano-4	Salicylic acid / behenic acid	Amide
FunzioNano-5	Glycidyl methacrylate	Tertiary amine / acrylic cross-linking
FunzioNano-6	1) Glycidyl 2,2,3,3,4,4,5,5-octafluoropentyl ether 2) Hexanoic acid	Tertiary amine / amide
FunzioNano-7	1) 3,5 Difluorbenzoic acid 2) Hexanoic acid	Amide
FunzioNano-8	neo-Decanoic acid	Amide
FunzioNano-9	10-Undecenoic acid	Amide / olefin cross-linking
FunzioNano-10	Behenic acid	Amide
FunzioNano-11	Erucic acid	Amide / olefin cross-linking
FunzioNano-12	t-Butylphenylgycidylether	Tertiary amine / hotmelt properties

The products are registered under the trademark FunzioNano®. Amine-POSS has been prepared as described above in synthesis step 1. The reactants have been added similar to the procedure described in synthesis step 2.
The most important factor of the manufacturing costs is the price of the silane. A typical industrial bulk price for 3-aminopropyltriethoxy silane is currently 6 EUR/kg. The reactants are normally less expensive and contribute with 1-2 EUR/kg. Typical manufacturing costs based on the raw materials of the FunzioNano® in Table 1 are about 4 EUR/kg.

Gas barrier properties of polymer nanocomposite coatings based on POSS

The gas barrier properties of polymer materials are very much influenced by the presence of aromatic moieties, polar groups such as hydroxyl groups and the degree of cross-linking. The oxygen transmission rate (OTR) of the aromatic polyester polyethylene terephthalate (PET) is considerably lower as the OTR of the aliphatic polyester poly lactic acid (PLA). The OTR of the partial polar ethylene vinyl alcohol copolymers (EVOH) is significantly lower than the OTR of the non-polar polyethylene. Finally, the gas barrier properties of cross-linked polyethylene are superior to those of a similar non cross-linked polyethylene (Massey 2003).
FunzioNano-2 consists mainly of non-polar aliphatic hydrocarbon moieties resulting from the mixture of unsaturated fatty acids which have been used as reactant. Aliphatic hydrocarbon chains provide a low gas barrier. Table 2 shows that the presence of the amide bond does not significantly increase the barrier for oxygen or helium.

Table 2 Oxygen transmission rate (OTR) and helium transmission rate (HeTR) in a film of FunzioNano-2 compared to commercial materials with similar functional groups

Material	OTR [cm³*20µm/m²*day]	HeTR [cm³*20µm/m²*day]	Rel. Humidity [%][3]
LLDPE	18200[1]	36900[1]	0 / 0
LDPE	12000[2]	28000[2]	0 / 0
PA-66 (non-oriented)	40[2]	2960[2]	50 / 50
PA-12 (BOPA-12)	43[1]	2306[1]	50 / 0
FunzioNano-2	4650[1]	49000[1]	0 / 0

[1] Measured with the methods described in "Experimental Section. Gas barrier measurements"
[2] (Massey 2003)
[3] The first number refers to OTR and the second number refers to HeTR

A better barrier against oxygen can be achieved by applying a mixture of FunzioNano-3 and FunzioNano-5 to a thermoplastic surface and subsequent curing (48 h, 60 °C). The application of the FunzioNano® mixture as a barrier coating (thickness: 20 µm) onto a compression moulded HDPE sample (film thickness: 120 µm) reduces the OTR from 150 cm³/m²*day to 8 cm³/m²*day (Fig. 8).
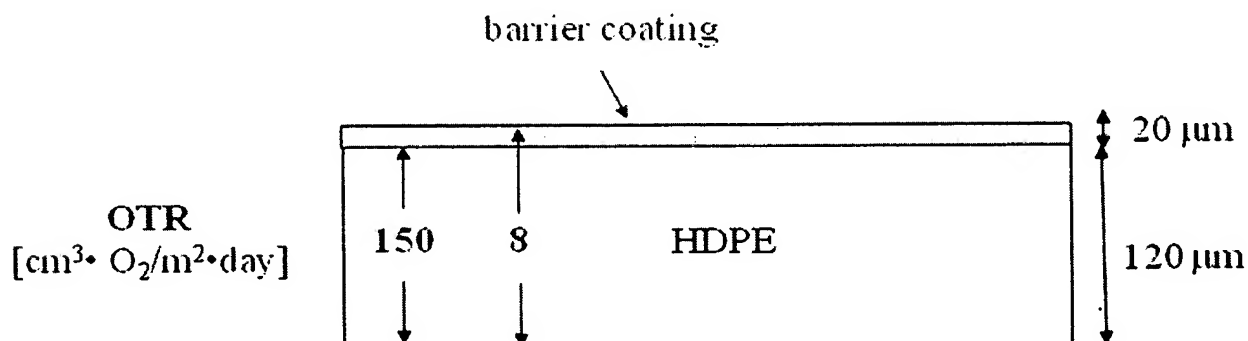

Fig. 8 OTR of a FunzioNano® coated HDPE film

FunzioNano-3 contains aromatic moieties, amide bonds and hydroxyl groups. FunzioNano-5 contains hydroxyl groups and acrylic double bonds which are cross-linked during the curing procedure.
The use of amine-POSS as cross-linking agent in epoxy systems (Table 3) can increase the cross-linking density. The hardener component of the selected epoxy resin is modified by amine-POSS. Stoichiometric mixing ratios were used. All components are mixed by moderate agitation and the ready-to-handle resins are applied by tape casting on non-adherent polymer substrates in wet film thickness of 200µm. The very smooth coating layers are cured under ambient conditions.

Table 3 Composition of modified epoxy samples: all components in [mass-%]

Sample	Resin Bisphenol-A MW 380 g/mole	Difunctional reactive diluent neopentyl glycol diglycidyl ether MW 216 g/mole	Amine hardener polyamine-adduct	Amine hardener amine-POSS
epoxy 1	65.1	0.0	28.7	6.2
epoxy 2	58.4	6.5	35.1	0.0
epoxy 3	57.9	6.4	29.4	6.3

Higher cross-linking density leads to an increased gas barrier. In addition, during cross-linking the reactive diluent yields more OH-groups per mass unit than the epoxy resin due to lower molecular weight. Thus, this increases the gas barrier properties.

He - transmission rates of epoxy films modified with nanoparticles acting as multifunctional crosslinker
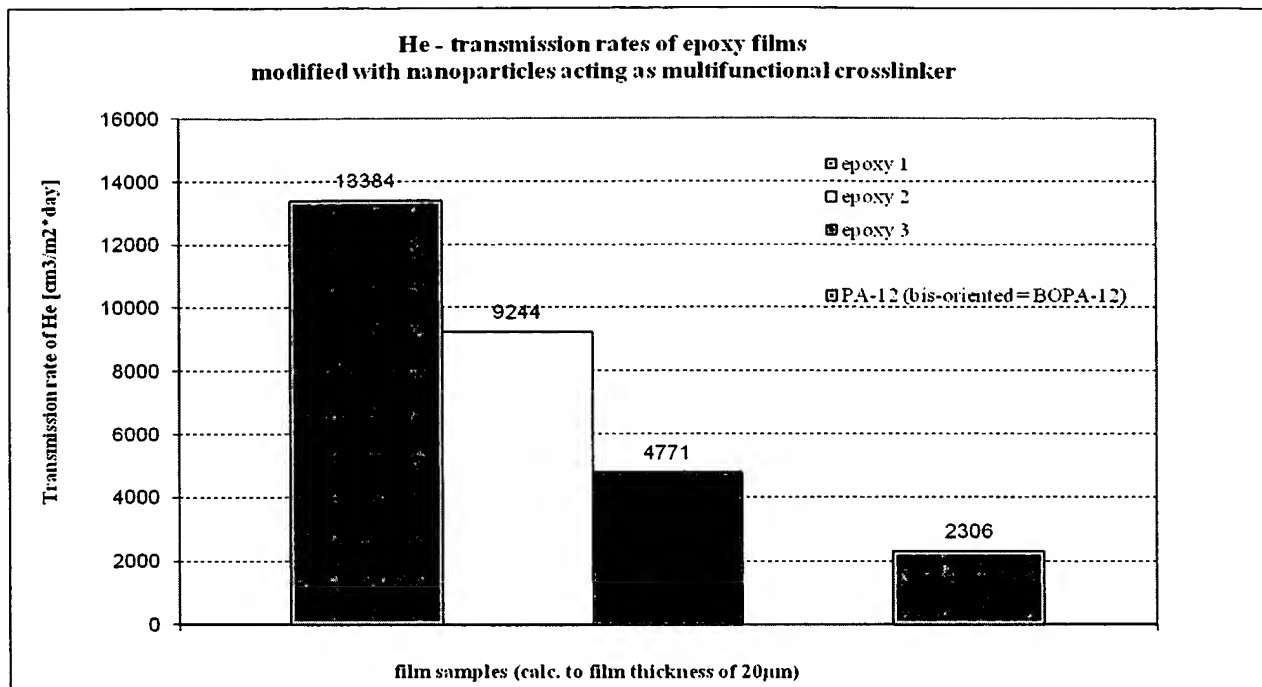
Fig. 9 HeTR of epoxy films containing amine-POSS

Highly cross-linked nanoparticle-modified epoxy coatings can give gas barrier properties close to the level of BOPA-12 (Fig. 9) and have good adhesion to a variety of substrate materials. This could make two layer flow pack barrier films such as epoxy coated bis-oriented polypropylene (BOPP) feasible. Additionally, the modified epoxy coatings show high transparency and excellent UV resistance (Pilz et al. 2009a).

Conclusions

It has been shown that a two step synthesis of modified POSS is feasible. The basic POSS structure with free amine groups is formed in the first step. The modification of these amine groups by using state-of-the-art amine chemistry is done in the second step without degrading the POSS structure. Therefore, a large variety of functionalized POSS compounds can be yield by this method. From an industrial point of view POSS products can be interesting components in polymer products if their benefit is not spoiled by too high manufacturing costs. The use of low cost organic commodities such as fatty acids decreases the manufacturing costs. Very recently, a POSS containing alkyd paint with reduced VOC and improved weathering resistance in northern climate has been introduced to the market. This would not have been possible with only silanes as raw materials for POSS synthesis.

Several types of POSS which were made by the two step synthesis have been applied in nanocomposite coatings. Gas barrier properties against oxygen and helium have been improved. Good adhesion to a variety of substrate materials combined with low gas transmission rates makes these POSS types to an interesting component in industrial packaging developments.

Summary

A large variety of functionalized POSS compounds can be synthesized by a two step method. The use of low cost organic commodities such as fatty acids decreases the manufacturing costs. Very recently, a POSS containing alkyd paint with reduced VOC and improved weathering resistance in northern climate has been introduced to the market. Good adhesion to a variety of substrate materials combined with low gas transmission rates makes nanocomposite coatings based on functionalized POSS to interesting components in industrial packaging developments.

Acknowledgments

Reference list

Amerio E, Sangermano M, Colucci G, Malucelli G, Messori M, Taurino R, Fabbri P (2008) UV Curing of Organic-Inorganic Hybrid Coatings Containing Polyhedral Oligomeric Silsesquioxane Blocks. Macromol Mater Eng 293: 700

Cordes DB, Lickiss PD, Rataboul F (2010) Recent Developments in the Chemistry of Cubic Polyhedral Oligosilsesquioxanes. Chem Rev 110: 2081–2173

dell' Erba IE, Fasce DP, Williams RJJ, Erra-Balsells R, Fukuyama Y, Nonami H (2003) Poly(silsesquioxanes) derived from the hydrolytic condensation of organotrialkoxysilanes containing hydroxyl groups. J Organomet Chem 686: 42

Fina A, Bocchini S, Camino G (2008) Catalytic fire retardant nanocomposites. Polym Degrad Stab 93: 1647

Glodek TE, Boyd SE, McAninch IM; LaScala JJ (2008) Properties and performance of fire resistant eco-composites using polyhedral oligomeric silsesquioxane (POSS) fire retardants. Comp Sci Tech 68: 2994

Haas K; Rose K (2003) Hybrid inorganic/organic polymers with nanoscale building blocks: precursors, processing, properties and applications. Rev Adv Mater Sci 5: 47

Helland T, Marstokk O, Männle F, Simon C.R, Yang J (2009) Binder for air-drying paint comprising nanoparticle organically modified metal oxides. WO2009113876

Iwamuraa T, Adachib K, Sakaguchia M, Chujo Y (2009) Synthesis of organic–inorganic polymer hybrids from poly(vinyl chloride) and polyhedral oligomeric silsesquioxane via CH/π interaction. Prog Org Coat 64: 124

Kannan RY, Salacinski HJ, Butler PE, Seifalian AM (2005) Polyhedral Oligomeric Silsesquioxane Nanocomposites: The Next Generation Material for Biomedical Applications. Acc. Chem. Res., 2005, 38 (11), 879-884

Kidane AG, Edirisinghe MJ, Bonhoeffer P, Seifalian AM (2007) Flow behaviour of a POSS biopolymer solution. Biorheology 44: 265

Kim EH, Myoung SW, Jung YG, Paik U (2009) Morphology and mechanical properties of PET by incorporation of amine-polyhedral oligomeric silsesquioxane. Prog Org Coat 64: 205

Kim KH-U,.Bang YH, Choi SM, Yoon KH (2008) Polyhedral oligomeric silsesquioxane-reinforced polyurethane acrylate. Comp Sci Tech 68: 2739

Li Q, Hutcheson SA, McKenna GB, Simon SL (2008) Viscoelastic Properties and Residual Stresses in Polyhedral Oligomeric Silsesquioxane-Reinforced Epoxy Matrices. Polym Sci Part B: Polym Phys 46: 2719

Lichtenhan JD, Otonari YA, Cam MJ (1995) Linear Hybrid Polymer Building Blocks: Methacrylate-Functionalized Polyhedral Oligomeric Silsesquioxane Monomers and Polymers. Macromolecules 28: 8435

Limbach HH (2007) Single and multiple hydrogen/deuterium transfer reactions in liquids and solids. In: Hynes JT, Klinman J, Limbach HH and Schowen RL (ed) Hydrogen Transfer Reactions, Wiley-VCH, Weinheim, Germany Vol. 1 pp 135–221 and references cited therein

Liu YR, Huang YD, Liu L (2008) Influence of Methacryl Polyhedral Oligomeric Silsesquioxane on the Thermal and Mechanical Properties of Methylsilicone Resin. J Appl Polym Sci 110: 2989

Mabry JM, Vij A, Iacono ST, Viers BD (2008) Fluorinated Polyhedral Oligomeric Silsesquioxanes (F-POSS). Angew Chem Int Ed 47: 4137

Männle F, Rødseth KR, Bu H (2005) Ligh protective additive based on organic/ inorganic hybrid polymer method for its manufacture and use thereof. WO2007053024

Männle F, Simon CR, Beylich J, Redford K (2004a) Polybranched, organic/ inorganic hybrid polymer and method for its manufacture. WO2005100449

Männle F, Simon CR, Beylich J, Larsen ÅG, Hauge RP, Kleppe EA, Rødseth KR (2004b) Polymer composition. WO2005100469

Männle F, Simon CR, Beylich J, Sommer B, Hinrichsen EL, Andreassen E, Olafsen K, Redford K, Didriksen T (2004c) Method for the manufacture of polybranched organic/ inorganic hybrid polymers. WO2005100450

Manson B.W, Morrison JJ, Coupar PI, Jaffrès P-A, Morris RE (2001) Synthesis of aldehyde functionalised polyhedral oligomeric silsesquioxanes. J Chem Soc Dalton Trans: 1123

Massey LK (2003) Permeability properties of Plastics and Elastomers: a guide to packaging and barrier materials. In: Massey LK (ed) Plastics Design Library, Norwich, NY, USA

Pilz M, Helland T, Simon CR, Yang J, Männle F, Bu H, Marstokk O (2009a) Epoxy coatings based on nanotechnology by using organic inorganic hybrid polymers. In: Proceedings of 19th SLF Congress, Sandefjord / Norway, 07.-08. Sep 2009

Pilz M, Männle F, Simon CR, Trevor SL, Bu H, Tanem BS (2009b) New Method for Improving Properties of Polymer Composites by Using Organic Inorganic Hybrid Polymers. Solid State Phenomena 151: 10-16

Sanchez-Soto M, Schiraldi DA, Illescas S (2009) Study of the morphology and properties of melt-mixed polycarbonate–POSS nanocomposites. Eur Polym J 45: 341

Schwab JJ, Lichtenhan JD (1998) Polyhedral Oligomeric Silsesquioxane (POSS)-Based Polymers. Appl Organometal Chem. 12: 707

Sheen Y-C, Lu C-H, Huang C-F, Kuo S-W, Chang F-C (2008) Synthesis and characterization of amorphous octakis-functionalized polyhedral oligomeric silsesquioxanes for polymer nanocomposites. Polymer 49: 4017

Smentkowski VS, Duong HM, Tamaki R, Keenan MR, Ohlhausen JAT and Kotula PG (2006) Appl Surf Sci 253: 1015

Su H-W, Chen W-C (2009) Preparation of nanoporous poly(methyl silsesquioxane) films using core-shell silsesquioxane as porogen. Mat Chem Phys 114: 736

Wan C, Zhao F, Bao X, Kandasubramanian B, Duggan M (2009) Effect of POSS on Crystalline Transitions and Physical Properties of Polyamide 12. J Polym Sci Part B: Polym Phys 47: 121

Wheeler PA, Fu BX, Lichtenhan JD, Weitao J, Mathias LJ (2002) Incorporation of Metallic POSS, POSS Copolymers, and New Functionalized POSS Compounds into Commercial Dental Resins. J Appl Polym Sci 102: 2856

Wu J, Patrick T (2009) POSS Polymers: Physical Properties and Biomaterials Applications. Mather Polym Rev 49: 25

Xiao Y, Lu X, Zhang X; He C (2010) Synthesis and optical characteristics of organic light-emitting dot based on well-defined octa-functionalized silsesquioxane. J Nanopart Res 12 (8): 2787-2798

Zhang H-X, Shin Y-J, Yoon K-B, Lee D-H (2009) Preparation and properties of propylene/POSS copolymer with rac-Et(Ind)2ZrCl2 catalyst. Eur Polym J 45: 40

Zhang L, Abbenhuis HCL, Yang Q, Wang Y-M, Magusin PCMM, Mezari B, van Santen RA, Li C (2007a) Mesoporous Organic–Inorganic Hybrid Materials Built Using Polyhedral Oligomeric Silsesquioxane Blocks. Angew Chem Int Ed 46: 5003

Zhang X, Huang Y, Wang T, Hu L (2007b) Effects of silsesquioxane coating structure on mechanical interfacial properties of carbon fibre/polyarylacetylene composites. J Mater Sci 42: 5264

Zhang Z, Gu A, Liang G, Ren P, Xie J, Wang X (2007c) Thermo-oxygen degradation mechanisms of POSS/epoxy nanocomposites. Polym Degrad Stab 92: 1986

Zhang Z, Liang G, Wang X (2007d) The effect of POSS on the thermal properties of epoxy. Polym Bull (Heidelberg, Germany) 58: 1013

Zhang Z, Liang G, Wang J, Ren P (2007e) Epoxy/POSS Organic–Inorganic Hybrids: Viscoelastic,Mechanical Properties and Micromorphologies. Polym Compos 28: 175

Zhou Z, Zhang Y, Zeng Z, Zhang Y J (2008) Properties of POSS-Filled Polypropylene: Comparison of Physical Blending and Reactive Blending. J Appl Polym Sci 110: 3745